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# A test of the Hirshfeld definition of atomic charges and moments

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**Summary.** The Hirshfeld population analysis scheme which carves the molecular density into atomic density contributions is tested. This method does not require a reference to basis sets or their respective locations, but is based on a different physical and mathematical footing. The advantage of this method is that, when the molecular deformation density converges to the true solution, the computed net charges will necessarily converge. This method also allows a straightforward definition for "local" moments. About 36 molecules have been used to compute the conventional Mulliken and Löwdin population analyses with STO3G, 6-311G** and Dunning–Hay split valence basis sets. These results have been compared to the estimates provided by the Hirshfeld model. The charges found in the Hirshfeld method are smaller than those from the other methods.

**Key words:** Hirshfeld population analysis – Molecular density – "Local" moments – Charges

## 1. Introduction

Electron population analysis remains one of the important properties for the interpretation of a typical quantum chemical calculation. Despite the popularity of the Mulliken [1] and Löwdin [2] populations, these methods have a tendency in some cases to yield peculiar assignments of net charges. Nevertheless, concepts such as atomic populations, hybridization, valence state, bond order, and promotion are very important to a chemist in the understanding of the nature of the chemical bond.

Normally, in a Mulliken population analysis, the components of the trace of the product $PS$, where $P$ is the charge density bond order matrix and $S$ is the overlap matrix, are computed. These elements are partially summed into contributions from basis functions centered at various sites. This partitioning is the root problem since a complete basis set cannot be meaningfully partitioned into atomic subsets. The Löwdin population analysis proceeds in a similar way, using $S^{1/2}PS^{1/2}$, and has the same difficulties.

The population analyses of Mulliken [1], Löwdin [2], Roby [3], and Mayer [4] have, to some extent in their definition, an arbitrary nature of partitioning the molecular density into atomic populations. Davidson [5] proposed that since basis functions were an artifact of the analytic Hartree–Fock methods, the Mulliken population should be done with the "atomic" orbitals obtained from the same basis set. This method leads to more realistic interpretation of the hybridization and atomic orbitals involved in the bonding, but the population analysis suffers from the same problems as the one due to Mulliken when extended valence sets (Rydberg orbitals) are included. Read and coworkers [6] proposed the use of atomic natural orbitals with similar fate. An attractive remedy was proposed by Bader and coworkers [7] which requires numerical integration. However, in their scheme, a linear superposition of neutral atomic densities is not resolved back to yield net populations of zero on each atomic site. Recently, Cioslowski [8] proposed a method based on atomic polar tensors. In this approach, the fractional charges were obtained by averaging over the components of the partial derivatives of the dipole moment with respect to the atomic coordinates. In this method, some of the charges estimated for Hartree–Fock densities of molecules with multiple bonds were quite large. Though this was attributed to an artifact of the HF density, it is felt that since the HF density is very close to the true density, the charges obtained by this method are either unreasonable or else they are very sensitive to correlation effects.

## 2. Population analysis model and local moments

Hirshfeld presented a technique for defining "atomic charge densities" in a molecule. Similar ideas are used in the density functional programs by Becke [10] and Yang [11]. We were inspired to test this technique to extract net atomic charges on a larger variety of molecules than considered by Hirshfeld.

One could define the net charges $q_A$ as:

$$q_A = Z_A - \int W_A(\boldsymbol{r})\varrho(\boldsymbol{r})\,d\boldsymbol{r} \tag{1}$$

where $\varrho(\boldsymbol{r})$ is the density of electrons, $Z_A$ is the charge on nucleus $A$, and $W_A(\boldsymbol{r})$ are some weights with the property that:

$$\sum W_A(\boldsymbol{r}) = 1 \tag{2}$$

and that they carve out the atomic charge at site $A$. If the weights are disjoint (i.e. $W_A$ is either 0 or 1, as prescribed by the Heaviside step function), then this reduces to partitioning space as done by Bader [7] and others. Hirshfeld chose to partition the charge at each point so that superimposed atomic densities will lead to zero net charges. Therefore, we need that $W_A(\boldsymbol{r})$ represent the atomic spherical density distribution:

$$W_A(\boldsymbol{r}) = \eta_A(r_A) \Big/ \sum_X \eta_x(r_x) \tag{3}$$

where $\eta_A(r)$ are accurate atomic densities.

Instead of Eq. (1), we define the deformation density $\Delta\varrho$ as:

$$\Delta\varrho = \varrho(\boldsymbol{r}) - \sum_X \varrho_X(r_x) \tag{4}$$

where the $\varrho_X(r)$ are the spherical neutral atom densities evaluated in the same molecular basis as $\varrho(r)$. Then we define the net charge:

$$q_A = -\int W_A(\boldsymbol{r})\,\Delta\varrho(\boldsymbol{r})\,d\tau \tag{5}$$

This will differ slightly from Eq. (1) if $\varrho_X$ differs from $\eta_X$.

It may be noted that $\eta_A(r)$ is a fixed, accurate atomic density. The molecular density and the atomic density $\varrho_A(r)$ are normally evaluated using a Gaussian basis. Thus this method is a simple way of softly carving out atomic density contributions from the molecular density. We note that since:

$$\int \Delta\varrho\,d\tau = 0 \tag{6}$$

we have

$$\sum q_A = 0 \tag{7}$$

In Fig. 1, we show the total charge density of $N_2$. Figure 2 shows Bader's definition of a nitrogen atom in this molecule, while Fig. 3 shows the result of using Hirshfeld's definition, $\varrho_A = W_A\varrho$. In Fig. 4, we show $\Delta\varrho$ for this molecule, while Fig. 5 shows the Hirshfeld distortion density for one atom, $\Delta\varrho_A = W_A\,\Delta\varrho$. The Hirshfeld definitions are visually pleasing.

Recently in a paper by Baerends et al. [12], various plots of $\Delta\varrho(\boldsymbol{r})$ were depicted for various basis sets. With improvement of basis set, $\Delta\varrho(\boldsymbol{r})$ will converge to $\Delta^{\circ}_{\varrho}(\boldsymbol{r})$, the true molecular deformation density. As a consequence, $q_A$ will also converge to $q^{\circ}_A$ the net atomic charge defined in Eq. (5). At convergence, this will also agree exactly with Eq. (1).

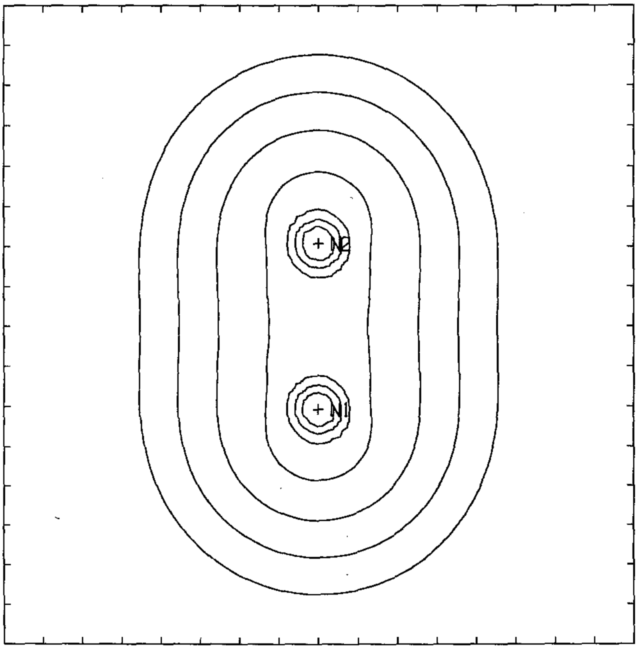

**Fig. 1.** A contour map of the total SCF electron density of $N_2$

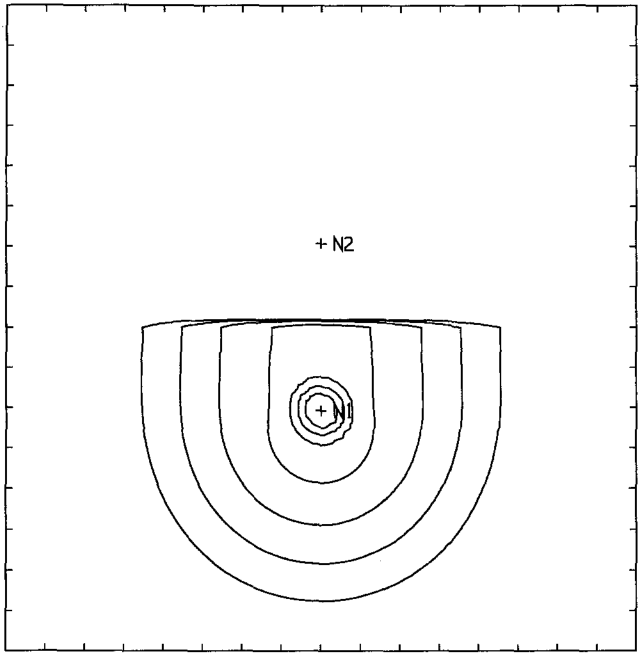

**Fig. 2.** The charge density of the nitrogen atom in $N_2$ using Bader's definition

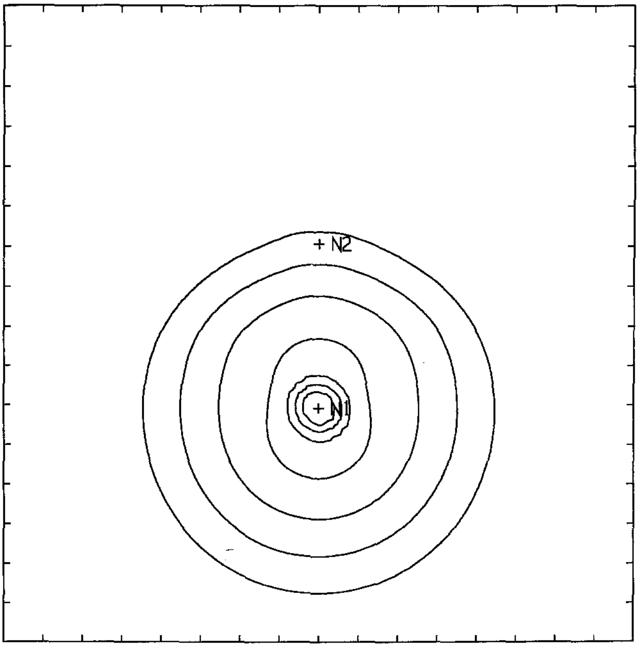

**Fig. 3.** The charge density of a nitrogen atom in $N_2$ using Hirshfeld's definition

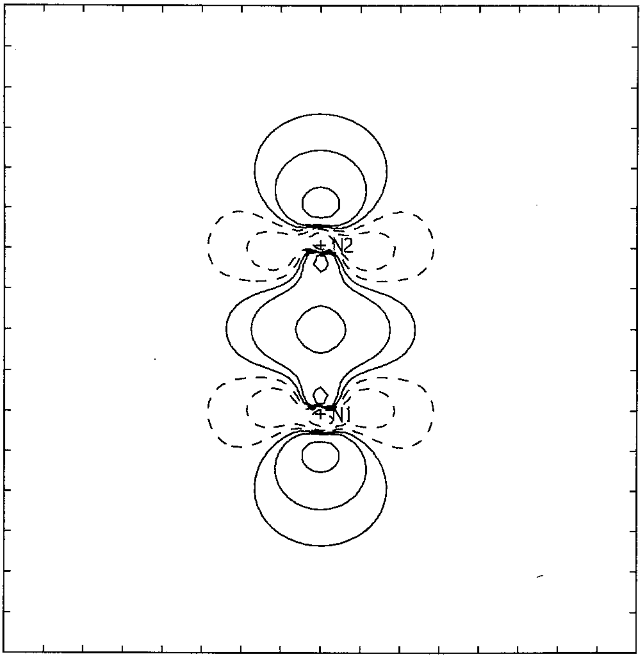

**Fig. 4.** The deformation density $\Delta\varrho$ for $N_2$ (see Eq. 4)

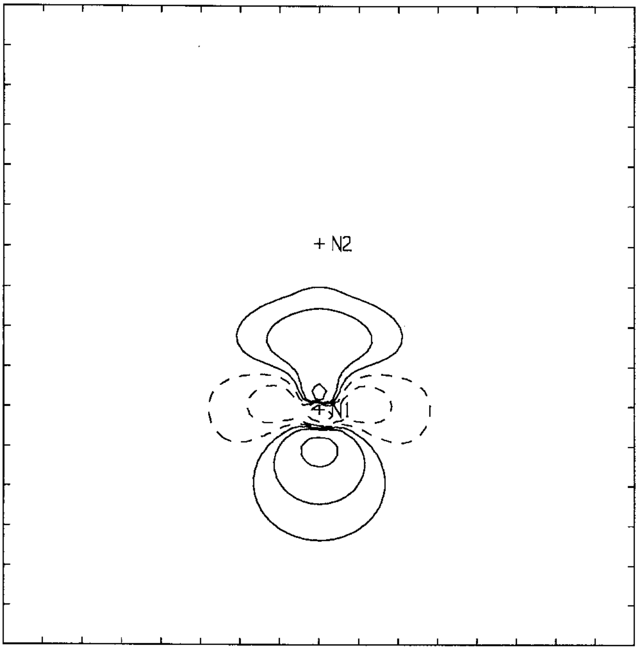

**Fig. 5.** The deformation density of a nitrogen atom in $N_2$ defined as $W_A \Delta\varrho$

We also define the "local" charge moments, e.g.:

$$\langle\langle x_A \rangle\rangle = -\int W_A(\boldsymbol{r}) x_A \, \Delta\varrho(\boldsymbol{r}) \, d\boldsymbol{r} \tag{8}$$

The components of the dipole moment of the molecule can be expressed as:

$$\mu_x = \sum (q_A A_x + \langle\langle x_A \rangle\rangle) \tag{9}$$

where $A_x$ is the $x$ coordinate of the atomic site $A$.

## 3. Computational considerations

In order to calculate $q_A$, we need $\varrho(\boldsymbol{r})$, $\varrho_A(r)$, $\eta_A(r)$ and a suitable three-dimensional numerical integration technique to evaluate Eq. (5). The molecular densities $\varrho(\boldsymbol{r})$ and the atomic densities $\varrho_A(r)$ are quantities which are evaluated for the respective basis for every $\boldsymbol{r}$ value. Instead of using numerical tabulations, we fit $\eta_A(r)$:

$$\eta_A(r) \simeq \sum C_i \exp(-\alpha_i r) \tag{10}$$

where $C_i$ and $\alpha_i$ are obtained by minimizing the standard deviation $S$:

$$S = \int \left[ \eta_A(r) - \sum C_i \exp(\alpha_i r) \right]^2 r^2 \, dr \tag{11}$$

subject to the constraint that the fitted density $\eta_A^\circ(r)$ satisfy normalization conditions. In our computation, we have used the HF data of Clementi and Roetti [13], however any numerical tabulation of $\eta_A(r)$ may be used. Since each integrand of Eqs. (5) and (8) is weighted heavily at the atomic site $A$ and $W_A(\boldsymbol{r})$ decays exponentially around center $A$, we prefer the use of spherical polar coordinates $r, \theta, \phi$ centered at $A$ as our variables of numerical integration. For numerical quadrature, we choose:

$$\int W_A \, \Delta\varrho(\boldsymbol{r}) \, d\tau \simeq \sum \sum \sum W_r W_\theta W_\phi \, \Delta\varrho(\boldsymbol{r}) \Big/ \sum \eta_x^\circ(r_x) \tag{12}$$

For the $\phi$ part, we choose an $2m$-point rule with equispaced points on a circle. For the $\theta$ part, we choose the $m$-point Gauss–Legendre rule. In case of the $r$ part, we use an $n$-point Gauss integration rule such that the $2n$ moments of the fitted atomic density $\eta_A^\circ(\boldsymbol{r})$ are conserved. In our integration scheme, we realize that with increasing $r$, a higher rule is needed for the $\theta$ and $\phi$ part and we use for "$M$" (the $m$-point rule) the empirical relation:

$$M = 2\pi r + 1.99999 \tag{13}$$

(with $M$ truncated to the next lower integer and $r$ in atomic units) so that the angular points maintain equal spacing as $r$ is increased.

## 4. Results and discussion

In Table 1, we have tabulated the net charges computed by the present algorithm and for comparison, we have also tabulated the corresponding Mulliken and Löwdin atomic charges. We note that the net charges computed with Eq. (5) are generally smaller in magnitude than the Mulliken net charges. For example, in

**Table 1.** Net atomic charges computed for listed molecules employing Mulliken (M), Lowdin (L), weighted space (P) populations

| Molecule | | STO3G | | | [3*s*2*p*] | | | 6-311G** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | M | L | P | M | L | P | M | L | P |
| AlH | Al | 0.41 | 0.36 | 0.33 | 0.43 | 0.33 | 0.21 | 0.34 | 0.29 | 0.18 |
| BeO | Be | 0.51 | 0.51 | 0.31 | 0.64 | 0.41 | 0.60 | 0.65 | −0.11 | 0.63 |
| BF | B | 0.18 | 0.01 | 0.03 | 0.24 | 0.06 | 0.10 | 0.18 | −0.35 | 0.13 |
| BH | B | 0.13 | 0.11 | 0.09 | 0.07 | 0.15 | 0.05 | 0.05 | 0.15 | 0.06 |
| PN | P | 0.48 | 0.36 | 0.28 | 0.61 | 0.51 | 0.29 | 0.39 | 0.34 | 0.28 |
| ClF | Cl | 0.02 | 0.01 | −0.05 | 0.33 | 0.27 | 0.11 | 0.35 | 0.27 | 0.13 |
| CO | C | 0.20 | 0.04 | 0.06 | 0.42 | 0.23 | 0.06 | 0.21 | −0.14 | 0.14 |
| CS | C | −0.12 | −0.13 | −0.04 | −0.86 | −0.41 | −0.20 | −0.12 | −0.28 | −0.00 |
| HCl | H | 0.17 | 0.12 | 0.15 | 0.14 | 0.00 | 0.16 | 0.15 | −0.09 | 0.16 |
| HF | H | 0.21 | 0.16 | 0.14 | 0.27 | 0.06 | 0.24 | 0.32 | −0.06 | 0.26 |
| LiCl | Li | 0.66 | 0.60 | 0.54 | 0.60 | 0.23 | 0.53 | 0.57 | −0.14 | 0.54 |
| LiF | Li | 0.40 | 0.38 | 0.34 | 0.67 | 0.48 | 0.61 | 0.71 | 0.09 | 0.63 |
| LiH | Li | 0.14 | 0.13 | 0.19 | 0.28 | 0.20 | 0.42 | 0.37 | 0.16 | 0.43 |
| SiO | Si | 0.49 | 0.37 | 0.35 | 0.89 | 0.68 | 0.51 | 0.60 | 0.39 | 0.47 |
| $CO_2$ | C | 0.49 | 0.33 | 0.34 | 1.12 | 0.46 | 0.42 | 0.70 | −0.40 | 0.46 |
| $C_3$ | C | 0.21 | 0.19 | 0.10 | 1.22 | 0.28 | 0.00 | −0.24 | −0.70 | −0.18 |
| | C′ | −0.11 | −0.09 | −0.05 | −0.61 | −0.14 | −0.00 | 0.12 | 0.35 | 0.09 |
| HCN | H | 0.15 | 0.11 | 0.10 | 0.74 | 0.15 | 0.18 | 0.23 | 0.03 | 0.15 |
| | C | 0.01 | −0.01 | 0.05 | −0.56 | −0.11 | −0.08 | 0.07 | −0.15 | 0.05 |
| | N | −0.16 | −0.09 | −0.15 | −0.18 | −0.03 | −0.10 | −0.30 | 0.12 | −0.20 |
| $H_2O$ | H | 0.19 | 0.13 | 0.11 | 0.22 | 0.05 | 0.18 | 0.25 | −0.05 | 0.18 |
| $H_2S$ | H | −0.04 | −0.05 | 0.01 | 0.04 | −0.04 | 0.08 | 0.04 | −0.10 | 0.08 |
| $N_2O$ | N | −0.37 | −0.38 | −0.30 | 0.03 | 0.10 | −0.32 | −0.03 | 0.07 | −0.08 |
| | N′ | 0.75 | 0.76 | 0.65 | 0.26 | 0.06 | 0.97 | 0.52 | −0.01 | 0.31 |
| | O | −0.39 | −0.39 | −0.35 | −0.29 | −0.16 | −0.65 | −0.49 | −0.06 | −0.22 |
| $O_3$ | O | 0.14 | 0.22 | 0.22 | 0.22 | 0.19 | 0.25 | 0.25 | 0.23 | 0.26 |
| | O′ | −0.07 | −0.11 | −0.11 | −0.11 | −0.09 | −0.12 | −0.12 | −0.11 | −0.13 |
| $H_2O_2$ | H | 0.20 | 0.14 | 0.12 | 0.26 | 0.05 | 0.20 | 0.29 | −0.06 | 0.19 |
| $NH_3$ | N | −0.47 | −0.31 | −0.23 | −0.44 | −0.12 | −0.99 | −0.56 | 0.10 | −0.31 |
| $NF_3$ | N | 0.17 | 0.13 | 0.12 | 0.53 | 0.19 | 0.25 | 0.67 | −0.01 | 0.32 |
| $PH_3$ | P | 0.30 | 0.30 | 0.14 | 0.15 | 0.27 | −0.05 | 0.18 | 0.35 | −0.06 |
| $C_2N_2$ | C | 0.10 | 0.04 | 0.10 | −0.06 | −0.10 | 0.02 | 0.26 | −0.25 | 0.13 |
| $CH_2O$ | C | 0.11 | 0.09 | 0.11 | −0.34 | 0.10 | −0.58 | 0.18 | −0.02 | 0.15 |
| | H | 0.05 | 0.02 | 0.02 | 0.34 | 0.09 | 0.33 | 0.08 | −0.01 | 0.06 |
| | O | −0.20 | −0.13 | −0.15 | −0.34 | −0.28 | −0.08 | −0.35 | 0.05 | −0.28 |
| $SiH_4$ | Si | 0.62 | 0.56 | 0.40 | 0.78 | 0.67 | 0.20 | 0.76 | 0.63 | 0.16 |
| $CH_4$ | C | −0.25 | −0.15 | −0.04 | −1.18 | −0.24 | −0.35 | −0.36 | 0.06 | −0.16 |
| $C_2H_2$ | C | −0.11 | −0.08 | −0.07 | −0.34 | −0.12 | −0.16 | −0.18 | −0.03 | −0.11 |
| $C_2H_4$ | C | −0.13 | −0.08 | −0.04 | −0.55 | −0.15 | −0.70 | −0.22 | 0.01 | −0.10 |
| $C_2H_6$ | C | −0.16 | −0.09 | −0.02 | −0.86 | −0.19 | −0.27 | −0.26 | 0.04 | −0.11 |
| $CH_3OH$ | C | −0.06 | −0.01 | 0.06 | −0.86 | 0.03 | −0.20 | 0.00 | 0.04 | −0.02 |
| | H | 0.07 | 0.04 | 0.02 | 0.35 | 0.06 | 0.10 | 0.09 | −0.03 | 0.05 |
| | $H_2$ | 0.05 | 0.02 | 0.01 | 0.32 | 0.04 | 0.09 | 0.07 | −0.04 | 0.04 |
| | O | −0.30 | −0.21 | −0.20 | −0.38 | −0.23 | −0.26 | −0.47 | 0.11 | −0.29 |
| | H | 0.19 | 0.13 | 0.11 | 0.24 | 0.07 | 0.19 | 0.24 | −0.05 | 0.18 |
| $(CH_3)_2S$ | C | −0.27 | −0.18 | −0.02 | −1.30 | −0.37 | −0.29 | −0.42 | −0.11 | −0.09 |
| | $H_3$ | 0.06 | 0.04 | 0.01 | 0.36 | 0.06 | 0.09 | 0.13 | −0.03 | 0.05 |
| | S | 0.15 | 0.14 | 0.00 | 0.45 | 0.39 | 0.01 | 0.10 | 0.39 | −0.13 |
| $B_2H_6$ | B | 0.08 | 0.02 | 0.10 | −0.17 | −0.06 | 0.02 | −0.06 | −0.13 | 0.03 |
| | $H_4$ | −0.04 | −0.04 | −0.06 | 0.04 | 0.00 | −0.04 | 0.01 | 0.01 | −0.04 |
| | $H_2$ | −0.01 | 0.05 | 0.03 | 0.08 | 0.06 | 0.05 | 0.04 | 0.11 | 0.05 |

$CH_4$ we see that the present model predicts a more covalent nature for the CH bond than the Mulliken and Löwdin analyses for all the basis sets. Also for $C_2H_4$ and $C_2H_6$, a smaller negative charge is predicted on the carbon in comparison to the Mulliken model. For the lithium compounds, LiH, LiF, and LiCl, we note that Mulliken population analysis predicts very similar net charges on Li atom and the same trend of increasing charge in the order LiH, LiCl, LiF.

The Hirshfeld atomic charge does change with basis sets as shown in the table. This is because these simple basis sets lead to quite different deformation densities. Therefore, it is necessary to compute accurate deformation densities in order to use any method reliably. Some of the previous criticism of the dependence of the Mulliken population on basis may, in fact, have been misdirected since wavefunctions are sensitive to basis for small basis sets. Table 2, for example, shows very

**Table 2.** Computed dipole moments

| Molecule | STO3G | | | [3*s*2*p*] | | | 6-311G** | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\mu_x$ | $\mu_y$ | $\mu_z$ | $\mu_x$ | $\mu_y$ | $\mu_z$ | $\mu_x$ | $\mu_y$ | $\mu_z$ |
| AlH | −0.50 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.10 | 0.00 | 0.00 |
| BeO | −0.96 | 0.00 | 0.00 | −2.87 | 0.00 | 0.00 | −2.82 | 0.00 | 0.00 |
| BF | 0.43 | 0.00 | 0.00 | 0.33 | 0.00 | 0.00 | 0.34 | 0.00 | 0.00 |
| BH | 0.38 | 0.00 | 0.00 | 0.75 | 0.00 | 0.00 | 0.67 | 0.00 | 0.00 |
| PN | −0.84 | 0.00 | 0.00 | −1.18 | 0.00 | 0.00 | −1.18 | 0.00 | 0.00 |
| ClF | 0.20 | 0.00 | 0.00 | −0.49 | 0.00 | 0.00 | −0.57 | 0.00 | 0.00 |
| CO | 0.07 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | −0.11 | 0.00 | 0.00 |
| CS | 0.37 | 0.00 | 0.00 | 0.93 | 0.00 | 0.00 | 0.57 | 0.00 | 0.00 |
| HCl | −0.68 | 0.00 | 0.00 | −0.71 | 0.00 | 0.00 | −0.56 | 0.00 | 0.00 |
| HF | −0.51 | 0.00 | 0.00 | −0.80 | 0.00 | 0.00 | −0.79 | 0.00 | 0.00 |
| LiCl | −2.67 | 0.00 | 0.00 | −3.05 | 0.00 | 0.00 | −2.89 | 0.00 | 0.00 |
| LiF | −1.26 | 0.00 | 0.00 | −2.45 | 0.00 | 0.00 | −2.51 | 0.00 | 0.00 |
| LiH | −0.94 | 0.00 | 0.00 | −2.35 | 0.00 | 0.00 | −2.36 | 0.00 | 0.00 |
| SiO | −0.75 | 0.00 | 0.00 | −1.58 | 0.00 | 0.00 | −1.37 | 0.00 | 0.00 |
| $CO_2$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| HCN | −0.96 | 0.00 | 0.00 | −1.11 | 0.00 | 0.00 | −1.27 | 0.00 | 0.00 |
| $H_2O$ | 0.00 | 0.00 | 0.68 | 0.00 | 0.00 | 0.95 | 0.00 | 0.00 | 0.85 |
| $H_2S$ | 0.00 | 0.00 | 0.40 | 0.00 | 0.00 | 0.70 | 0.00 | 0.00 | 0.53 |
| $N_2O$ | 0.03 | 0.00 | 0.00 | −0.40 | 0.00 | 0.00 | −0.28 | 0.00 | 0.00 |
| $O_3$ | −0.20 | 0.00 | 0.00 | −0.29 | 0.00 | 0.00 | −0.32 | 0.00 | 0.00 |
| $H_2O_2$ | 0.00 | 0.29 | 0.49 | 0.00 | 0.42 | 0.72 | 0.00 | 0.37 | 0.64 |
| $NH_3$ | 0.00 | 0.00 | 0.71 | 0.00 | 0.00 | 0.83 | 0.00 | 0.00 | 0.71 |
| $NF_3$ | 0.00 | 0.00 | 0.16 | 0.00 | 0.00 | −0.08 | 0.00 | 0.00 | −0.16 |
| $PH_3$ | 0.00 | 0.00 | 0.44 | 0.00 | 0.00 | 0.55 | 0.00 | 0.00 | 0.42 |
| $C_2N_2$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $CH_2O$ | −0.61 | 0.00 | −0.00 | −1.10 | 0.00 | 0.00 | −1.06 | 0.00 | 0.00 |
| $SiH_4$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $CH_4$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_2H_2$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_2H_4$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_2H_6$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_2H_6S$ | 0.39 | 0.00 | 0.00 | 0.75 | 0.00 | 0.00 | 0.71 | 0.00 | 0.00 |
| $CH_3OH$ | −0.31 | 0.50 | 0.00 | −0.57 | 0.69 | 0.00 | −0.45 | 0.60 | 0.00 |
| $B_2H_6$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 3.** Local moments for some molecules[b]

| Molecule | | | | STO3G | | [3$s$2$p$] | | 6-311G** | |
|---|---|---|---|---|---|---|---|---|---|
| | | | coor[a] | $\langle\langle r\rangle\rangle$ | $qR$ | $\langle\langle r\rangle\rangle$ | $qR$ | $\langle\langle r\rangle\rangle$ | $qR$ |
| $H_2$ | H | $x$ | 0. | −0.059 | 0. | −0.134 | 0. | −0.135 | 0. |
| AlH | Al | $x$ | 0. | 0.594 | 0. | 0.806 | 0. | 0.700 | 0. |
| | H | $x$ | 3.114 | −0.070 | −1.021 | −0.144 | −0.656 | −0.039 | −0.560 |
| BeO | Be | $x$ | 0. | −0.135 | 0. | −1.280 | 0. | −1.334 | 0. |
| | O | $x$ | 2.515 | −0.049 | −0.773 | −0.076 | −1.517 | 0.102 | −1.585 |
| BF | B | $x$ | 0. | 0.707 | 0. | 0.602 | 0. | 0.640 | 0. |
| | F | $x$ | 2.387 | −0.192 | −0.082 | −0.037 | −0.238 | −0.003 | −0.299 |
| BH | B | $x$ | 0. | 0.631 | 0. | 0.813 | 0. | 0.748 | 0. |
| | H | $x$ | 2.329 | −0.038 | −0.217 | 0.062 | −0.124 | 0.057 | −0.139 |
| PN | P | $x$ | 0. | 0.271 | 0. | 0.004 | 0. | −0.291 | 0. |
| | N | $x$ | 2.670 | −0.371 | −0.742 | −0.407 | −0.774 | −0.145 | −0.741 |
| ClF | Cl | $x$ | 0. | 0.226 | 0. | 0.085 | 0. | −0.008 | 0. |
| | F | $x$ | 3.077 | −0.180 | 0.151 | −0.238 | −0.332 | −0.165 | −0.398 |
| CO | C | $x$ | 0. | 0.461 | 0. | 0.351 | 0. | 0.223 | 0. |
| | O | $x$ | 2.132 | −0.268 | −0.128 | −0.190 | −0.132 | −0.023 | −0.308 |
| CS | C | $x$ | 0. | 0.477 | 0. | 0.382 | 0. | 0.278 | 0. |
| | S | $x$ | 2.901 | −0.212 | −0.105 | −0.024 | −0.571 | 0.278 | 0.010 |
| HCl | H | $x$ | 0. | −0.065 | 0. | −0.196 | 0. | 0.043 | 0. |
| | Cl | $x$ | 2.408 | −0.247 | −0.371 | −0.135 | −0.376 | −0.220 | −0.386 |
| HF | H | $x$ | 0. | −0.086 | 0. | −0.235 | 0. | −0.265 | 0. |
| | F | $x$ | 1.732 | −0.175 | −0.246 | −0.141 | −0.424 | −0.085 | −0.445 |
| LiCl | Li | $x$ | 0. | −0.431 | 0. | −0.947 | 0. | −0.987 | 0. |
| | Cl | $x$ | 3.819 | −0.157 | −2.088 | −0.067 | −2.039 | 0.153 | −2.054 |
| LiF | Li | $x$ | 0. | −0.195 | 0. | −0.613 | 0. | −0.672 | 0. |
| | F | $x$ | 2.988 | −0.033 | −1.027 | −0.012 | −1.832 | 0.051 | −1.894 |
| LiH | Li | $x$ | 0. | −0.397 | 0. | −1.114 | 0. | −1.111 | 0. |
| | H | $x$ | 3.015 | 0.019 | −0.564 | 0.023 | −1.257 | 0.033 | −1.280 |
| SiO | Si | $x$ | 0. | 0.490 | 0. | 0.214 | 0. | 0.044 | 0. |
| | O | $x$ | 2.853 | −0.235 | −1.005 | −0.332 | −1.459 | −0.073 | −1.342 |
| $CO_2$ | O | $x$ | 2.144 | −0.266 | −0.366 | −0.287 | −0.448 | −0.081 | −0.489 |
| $C_3$ | C | $x$ | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| | C′ | $x$ | 2.419 | 0.720 | −0.122 | 0.923 | −0.001 | −0.248 | 0.216 |
| HCN | H | $x$ | −2.067 | −0.079 | −0.203 | −0.249 | −0.370 | −0.205 | −0.316 |
| | C | $x$ | −0.058 | −0.089 | −0.003 | −0.048 | 0.004 | −0.227 | −0.003 |
| | N | $x$ | 2.125 | −0.268 | −0.319 | −0.226 | −0.217 | −0.094 | −0.426 |
| $H_2O$ | O | $z$ | 0.0 | 0.315 | 0. | 0.259 | 0. | 0.166 | 0. |
| | H | $x$ | 1.428 | 0.058 | 0.161 | 0.179 | 0.258 | 0.182 | 0.253 |
| | | $z$ | 1.096 | 0.059 | 0.124 | 0.148 | 0.198 | 0.147 | 0.194 |
| $H_2S$ | S | $z$ | 0. | 0.349 | 0. | 0.249 | 0. | 0.038 | 0. |
| | H | $x$ | 1.849 | 0.009 | 0.012 | 0.115 | 0.143 | 0.138 | 0.153 |
| | | $z$ | 1.745 | 0.013 | 0.012 | 0.088 | 0.135 | 0.102 | 0.144 |
| $N_2O$ | N | $x$ | 0. | 0.380 | 0. | −0.283 | 0. | 0.138 | 0. |
| | N′ | $x$ | 2.127 | 0.065 | 1.375 | 0.298 | 2.065 | 0.134 | 0.660 |
| | O | $x$ | 4.369 | −0.287 | −1.510 | 0.368 | −2.843 | −0.185 | −1.022 |
| $O_3$ | O | $x$ | 0. | −0.314 | 0. | −0.275 | 0. | −0.152 | 0. |
| | O′ | $x$ | −1.277 | 0.114 | 0.142 | 0.122 | 0.159 | 0.069 | 0.168 |
| | | $z$ | 2.050 | −0.194 | −0.227 | −0.239 | −0.254 | −0.140 | −0.269 |
| $H_2O_2$ | O | $x$ | 0. | 0.178 | 0. | 0.232 | 0. | 0.167 | 0. |
| | | $y$ | 0. | 0.247 | 0. | 0.204 | 0. | 0.134 | 0. |
| | | $z$ | 0. | −0.009 | 0. | −0.020 | 0. | −0.010 | 0. |
| | H | $x$ | −0.317 | −0.015 | −0.038 | −0.059 | −0.062 | −0.062 | −0.061 |
| | | $y$ | 1.796 | 0.081 | 0.217 | 0.230 | 0.353 | 0.232 | 0.347 |
| | | $z$ | 0. | 0. | 0. | 0.001 | 0. | 0.002 | 0. |

**Table 3.** (continued)

| Molecule | | | | STO3G | | $[3s2p]$ | | 6-311G** | |
|---|---|---|---|---|---|---|---|---|---|
| | | | coor[a] | $\langle\langle r\rangle\rangle$ | $qR$ | $\langle\langle r\rangle\rangle$ | $qR$ | $\langle\langle r\rangle\rangle$ | $qR$ |
| $NH_3$ | N | $z$ | 0. | 0.403 | 0. | 0.014 | 0. | 0.231 | 0. |
| | H | $y$ | 1.764 | 0.067 | 0.138 | 0.262 | 0.580 | 0.176 | 0.185 |
| | H | $z$ | 0.735 | 0.046 | 0.058 | 0.032 | 0.242 | 0.082 | 0.077 |
| $NF_3$ | N | $z$ | 0. | 0.498 | 0. | 0.446 | 0. | 0.351 | 0. |
| | F | $y$ | 2.331 | −0.146 | −0.093 | −0.171 | −0.198 | −0.111 | −0.244 |
| | | $z$ | 1.129 | −0.068 | −0.045 | −0.080 | −0.096 | −0.051 | −0.118 |
| $PH_3$ | P | $z$ | 0. | 0.594 | 0. | 0.486 | 0. | 0.340 | 0. |
| | H | $y$ | 2.476 | 0.003 | −0.116 | 0.106 | 0.042 | 0.129 | 0.052 |
| | | $z$ | 1.033 | −0.002 | −0.049 | 0.003 | 0.018 | 0.005 | 0.022 |
| $C_2N_2$ | C | $x$ | 0. | 0.106 | 0. | 0.093 | 0. | 0.248 | 0. |
| | N | $x$ | −2.186 | 0.267 | 0.224 | 0.179 | 0.046 | 0.071 | 0.285 |
| $CH_2O$ | C | $x$ | 0.000 | 0.073 | 0.000 | 0.118 | 0.000 | 0.034 | 0.000 |
| | H | $x$ | −1.126 | −0.026 | −0.021 | −0.117 | −0.368 | −0.064 | −0.072 |
| | | $y$ | −1.990 | 0.054 | −0.037 | −0.250 | −0.651 | −0.117 | −0.127 |
| | O | $x$ | 2.287 | −0.241 | −0.346 | −0.074 | −0.175 | −0.121 | −0.629 |
| $SiH_4$ | H | $x$ | 2.796 | −0.010 | −0.279 | 0.048 | −0.136 | 0.088 | −0.113 |
| $CH_4$ | H | $x$ | 2.066 | 0.055 | 0.021 | 0.192 | 0.182 | 0.140 | 0.081 |
| $C_2H_2$ | C | $x$ | 0. | −0.164 | 0. | −0.184 | 0. | −0.264 | 0. |
| | H | $x$ | 4.280 | 0.074 | 0.299 | 0.226 | 0.693 | 0.206 | 0.487 |
| $C_2H_4$ | C | $x$ | 0. | −0.040 | 0. | −0.238 | 0. | −0.097 | 0. |
| | H | $x$ | −0.919 | −0.016 | −0.018 | −0.156 | −0.322 | −0.065 | −0.048 |
| | | $y$ | 1.803 | 0.055 | 0.035 | 0.332 | 0.632 | 0.151 | 0.094 |
| $C_2H_6$ | C | $x$ | 0. | 0.029 | 0. | 0.070 | 0. | 0.058 | 0. |
| | H | $x$ | −0.693 | −0.013 | −0.004 | −0.052 | −0.063 | −0.033 | −0.025 |
| | | $y$ | 1.964 | 0.051 | 0.010 | 0.179 | 0.178 | 0.133 | 0.070 |
| $CH_3OH$ | C | $x$ | 0. | 0.085 | 0. | 0.140 | 0. | 0.109 | 0. |
| | | $y$ | 0. | 0.001 | 0. | 0.002 | 0. | 0.000 | 0. |
| | H | $x$ | −0.611 | −0.015 | −0.010 | −0.061 | −0.063 | −0.048 | −0.032 |
| | | $y$ | 1.975 | 0.049 | 0.032 | 0.193 | 0.205 | 0.139 | 0.104 |
| | H′ | $x$ | −0.775 | −0.017 | −0.004 | −0.078 | −0.067 | −0.058 | −0.029 |
| | | $y$ | −0.927 | −0.022 | −0.005 | −0.081 | −0.080 | −0.058 | −0.035 |
| | | $z$ | −1.677 | −0.036 | −0.009 | −0.151 | −0.145 | −0.107 | −0.063 |
| | O | $x$ | 2.685 | −0.175 | −0.539 | −0.262 | −0.706 | −0.166 | −0.783 |
| | | $y$ | 0. | −0.251 | 0. | −0.203 | 0. | −0.124 | 0. |
| | H | $x$ | 3.248 | 0.021 | 0.361 | 0.049 | 0.622 | 0.067 | 0.581 |
| | | $y$ | −1.731 | −0.080 | −0.192 | −0.229 | −0.331 | −0.225 | −0.310 |
| $(CH_3)_2S$ | S | $x$ | 0. | 0.383 | 0. | 0.459 | 0. | 0.225 | 0. |
| | C | $x$ | 2.214 | −0.043 | −0.054 | −0.072 | −0.642 | −0.044 | −0.199 |
| | | $y$ | 2.587 | −0.044 | −0.063 | −0.087 | −0.750 | −0.052 | −0.232 |
| | H | $x$ | 4.169 | 0.051 | 0.051 | 0.186 | 0.404 | 0.140 | 0.227 |
| | | $y$ | 1.935 | −0.021 | 0.023 | −0.052 | 0.188 | −0.044 | 0.106 |
| | H′ | $x$ | 1.872 | −0.012 | 0.012 | −0.040 | 0.175 | −0.035 | 0.093 |
| | | $y$ | 3.728 | 0.028 | 0.024 | 0.111 | 0.349 | 0.082 | 0.186 |
| | | $z$ | 1.682 | 0.043 | 0.011 | 0.159 | 0.158 | 0.119 | 0.084 |
| $B_2H_6$ | H | $x$ | 0. | −0.031 | 0. | −0.134 | 0. | −0.111 | 0. |
| | | $y$ | 0. | −0.003 | 0. | 0.004 | 0. | 0.002 | 0. |
| | B | $x$ | 2.270 | 0.077 | 0.229 | 0.016 | 0.045 | −0.004 | 0.075 |
| | | $y$ | 0. | −0.136 | 0. | −0.028 | 0. | 0.007 | 0. |
| | H′ | $x$ | 3.090 | 0.000 | 0.085 | 0.000 | 0.159 | 0.000 | 0.151 |
| | | $y$ | −1.450 | 0.000 | −0.040 | 0.000 | −0.075 | 0.000 | −0.071 |
| | | $z$ | 1.856 | −0.006 | 0.051 | 0.179 | 0.096 | 0.168 | 0.091 |

[a] Atomic coordinates in Bohr

[b] All values are in a.u. $qR$ is the $q_A A_x$ term in Eq. (9), while $\langle\langle r\rangle\rangle$ is the $\langle\langle X_A\rangle\rangle$ term.

large changes in the total dipole moment between STO-3G and better basis sets. The dipole moment does not change much between the [3*s*2*p*] basis and the 6-311G** basis. The large difference in net charges found between these bases with the Mulliken and Löwdin methods reflect the breakdown of these methods when extended basis sets are used.

In Table 3, we have tabulated the non-zero local moments for the symmetry unique atoms of the molecule. These results illustrate the large contribution to the dipole moment from hybridization of lone pair orbitals in molecules like $NH_3$, BF, BeO, and BH. One can see that the small dipole moment in CO comes from a near cancellation between the charge transfer term and the large moment of the sigma lone pair on carbon. In CS, where the charge transfer part is smaller, the sigma lone pair moment on carbon dominates. Similarly, the large dipole moment in $NH_3$ compared to $NF_3$ is caused by the fact that the lone pair moment of N has the same sign as the charge transfer moment in $NH_3$, but the opposite sign in $NF_3$. Somewhat more surprisingly, but already mentioned in the literature [14], is the large local moment on H in most compounds which corresponds to the fact that the center of charge is not at the nucleus. For Li containing compounds, this effect is even larger and not as well documented.

The Hirshfeld method is also arbitrary. One of the arbitrary choices was referencing all density differences to the neutral atoms. Hartree–Fock anion densities are not very suitable for use because they are very diffuse. But as a test of the robustness of the method we have tried calculating the charges in $N_2$ using $N^+N^-$ as the reference density both in computing the weights and in forming $\Delta\varrho$. The resulting charges were $N^{+0.54}N^{-0.54}$. Thus, the Hirshfeld method is somewhat dependent on the initial charges assumed. An even less fair test is to calculate the charges in BeO using $Be^{2+}O^{2-}$ as the reference density since this has no valence electrons on Be and the effective volume is just the space occupied by the core electrons. This choice gave $Be^{1.1}O^{-1.9}$ for the charges because little of $\Delta\varrho$ is in the same region of space as the $Be^{2+}$ charge density.

Since the Hirshfeld method seems to underestimate charges, it might be useful to define weights and $\Delta\varrho$ bases on fractional charges. If these could be iterated to self-consistency, somewhat larger charges would be obained. To do this, interpolated densities for fractional charges would be needed.

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